

**BELLCOMM, INC.**

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**SUBJECT:** Electron Delocalization and  
Aromaticity: Their Effect on the  
Thermal Stability of Polymeric  
Materials - Case 320

**DATE:** September 20, 1968**FROM:** M. V. Drickman**ABSTRACT**

The requirement for a safe, fire-resistant environment in isolated, manned vehicles such as submarines and spacecraft, has given fresh impetus to the search for thermally stable polymers. The empirical search for these materials has centered about polymers which contain aromatic substituents in the carbon backbone. Aromaticity is a special case of the phenomenon known as electron delocalization.

This memorandum presents a physical picture of electron delocalization and aromaticity and explains why these phenomena are fundamental to the enhanced thermal stability of polymeric materials which contain aromatic groups in the carbon backbone. Some differences between the properties of simple aromatic and non-aromatic compounds are explained. Examples of aromatic polymers are given and their thermal behavior is compared with non-aromatic materials.

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AROMATICITY THEIR EFFECT ON THE THERMAL  
STABILITY OF POLYMERIC MATERIALS (Bellcomm,  
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MEMORANDUM FOR FILE

## INTRODUCTION

At present there is a need to develop nonmetallic materials (specifically polymers) which remain stable when exposed to temperature extremes for extended time periods. In addition to chemical stability it is desirable that these materials retain both their physical and mechanical properties at temperatures above 500°C (932°F).

Theoretically, chemical behavior can be predicted from considerations of molecular geometry, i.e., stereochemical effects. This approach has been successfully applied in the design of freon cooling agents, and efforts are being initiated to define and understand these stereochemical effects in polymers. At present, however, there are insufficient data to logically predict the proper configurations for incorporation into polymer systems. Thus, most effort to date has been of an empirical nature.

The empirical search for thermally stable materials has centered about the following types of polymeric systems:<sup>[9]</sup>

1. Polymers with aromatic groups in the backbone.  
(Aromaticity - the major subject of this memorandum - is explained in the next section.)
2. Polymers with heterocyclic groups in the backbone.  
(Heterocyclic groups are rings containing two or more different atomic species.)
3. Polymers with chelate groups in the backbone.  
(Chelate groups are rings which share a central atom.)
4. Polymers with silicon in the backbone.  
(These are commonly called silanes.)
5. Polymers with organo-metallic groups in the backbone.  
(Organo-metallic groups consist of a metal (or metals) bonded to organic groups.)
6. Polymers built from inorganic monomers.  
(These are called inorganic polymers.)

In long range terms the inorganic polymers appear to be the most promising since inorganic molecules are generally more thermally stable than organic molecules and this behavior should also exist in more complex polymeric systems. However, at present, although inorganic monomers and their low molecular weight polymers have been made, the conversion to high molecular weight polymers has not been successful. The ability to synthesize high molecular weight polymers is quite important since for all known organic polymers good plastic properties are achieved only with high molecular weights and crystallinity. The molecular weights of most commonly used fibers vary between  $10^4$  and  $2 \times 10^5$ ; a molecular weight of  $1.5 \times 10^5$  is usually needed before fibers can be drawn.

Polymers containing aromatic groups in the backbone are of greatest current interest. Aromaticity is a result of the phenomenon known as electron delocalization and the intent here is to explain this phenomenon. In all cases electron delocalization has been found to have a profound effect on the chemical, physical, and mechanical properties of polymers; for example, empirical evidence indicates that the thermal stability and electron delocalization are directly related.<sup>[9]</sup> Polymers which exhibit thermal stability are generally non-flammable, since it is the pyrolysis products which are the actual combustibles.<sup>[2]</sup> If the production of flammable pyrolysis products can be minimized, the fire hazard is decreased.

This memorandum explains the thermal stability and flammability properties of aromatic polymers in terms of chemical structure. Such an understanding of the relationship between the chemical structure and these properties should be helpful in the development of suitable criteria for new materials design and selection.

#### ELECTRON DELOCALIZATION AND AROMATICITY

It was demonstrated over forty years ago that electrons behave both as particles and waves. Since electrons have wave properties it is possible to describe electrons and atoms in terms of  $\psi$ , a wave function.<sup>[3,4,6,7]</sup>

By means of the Schrödinger equation it is possible to relate the energy of an atomic system to the electron's wave motion, by the relationship  $H\psi = E\psi$ . The Hamiltonian operator  $H$  represents the general form of kinetic and potential energies of the system;  $E$  is the numerical value for the energy of any particular  $\psi$ . The probability of finding an electron in any volume element in space is proportional to the square of the absolute value of the wave function, integrated over that volume of space; this is the physical significance of the wave function.

The Schrödinger equation is a very complex differential equation and only very simple systems yield exact solutions; the hydrogen atom is one of these systems. The solutions for the hydrogen atom are commonly called hydrogenic orbitals. The Schrödinger equation does not yield exact solutions for other atoms, and therefore the hydrogenic orbitals are used as approximations to describe these atoms.

A discussion of polymeric materials and a qualitative scheme of polymer combustion have already been presented.<sup>[2]</sup> The pyrolysis reaction was shown to be very important in relation to both thermal decomposition and combustion and it was indicated that the presence of "aromatic" groups in the carbon backbone of the polymer resulted in an enhancement of the thermal stability. We will now consider the wave mechanical implications of such aromaticity.

Elemental carbon contains six electrons which are located in the hydrogenic orbitals designated as 1s, 2s, and 2p. Figure 1 illustrates the electron distribution in these orbitals. More specifically, the electronic configuration of carbon can be represented as  $1s^2 2s^2 2p^2$ , i.e., there are two electrons associated with each orbital.

Classical bonding theory can explain only di-valent carbon bonding. However, tri- and tetra-valent carbon compounds also exist. This behavior can be explained if we construct linear combinations of the hydrogenic atomic orbitals. These linear combinations of orbitals, called hybrids, will result in cases corresponding to di-, tri-, and tetra-valent carbon. Acetylene,  $HC \equiv CH$  is an example of di-valency, ethylene (or ethene),  $H_2C = CH_2$  is an example of tri-valency, and methane,  $CH_4$ , of tetra-valency.

Since our concern is with the enhancement of molecular stability due to the delocalization of electrons in a molecule, specifically the phenomenon known as aromaticity, it is necessary (for reasons which will be explained below) to consider only the case in which carbon is tri-covalent (bonded to three other atoms) and exhibits trigonal, planar geometry. Tri-valent carbon is a result of the formation of  $sp^2$  hybrid orbitals. Figure 2<sup>[1]</sup> illustrates the  $sp^2$  orbitals. The calculations in which the orbitals are derived also provide us with information concerning the geometry, namely, that the orbitals are directed to the corners of an equilateral triangle and when bonds are eventually formed the resulting configuration will be trigonal and planar.

Chemical bonds are formed when these orbitals overlap colinearly with orbitals of other atoms. These bonds, called

$\sigma$ -bonds, control the molecular geometry. In the case of  $sp^2$  orbitals there is an unpaired p electron remaining in an atomic orbital directed perpendicularly to the plane of the  $\sigma$ -bond. If the atom containing the unpaired electron bonds with another carbon atom in a similar situation, the p orbitals will overlap and another bond will be formed; such bonds, called  $\pi$  bonds, are not as strong as the  $\sigma$ -bonds. Figure 3 illustrates overlap of p orbitals resulting in  $\pi$  bonding.

The phenomenon known as conjugation occurs when there are  $\pi$  bonds on alternate pairs of carbon atoms ( $-C=C-C=C-$ ). Since electrons are indistinguishable from each other, it is impossible to differentiate between those associated with different  $\pi$  bonds in systems exhibiting conjugation. Physically, the result is a smearing out of the electron cloud over the molecule, a phenomenon known as electron delocalization. This situation adds to the overall stability of the molecule, as will be discussed in the next section.

In some cyclic molecules (e.g., benzene, pyridine) the effects of the delocalization are so profound that their chemistry is greatly different from that of ordinary  $\pi$ -bonded systems (commonly referred to as unsaturated hydrocarbons). Molecules exhibiting this enhanced effect are called aromatic.

Figure 4 illustrates delocalization in butadiene,  $CH_2=CH-CH=CH_2$  (a linear conjugated  $\pi$  system), and Figure 5 shows benzene,  $C_6H_6$  (a cyclic aromatic).<sup>[1]</sup> When the atoms are drawn together due to  $\sigma$ -bond formation the  $\pi$  orbitals overlap to form a continuous sheet above and below the plane of the carbons. The important factor here is that these  $\pi$  electrons are not localized in a particular bond or near a particular atom, but that they are free to move anywhere within the regions shown.

#### THE EFFECTS OF ELECTRON DELOCALIZATION ON THE INTERNAL ENERGY OF A MOLECULAR SYSTEM

An analogy with the "particle in a box" can be drawn to illustrate how electron delocalization results in stabilization due to a lowering of the internal energy of the molecular system.

If we think of an electron as either localized between two atoms or delocalized over a few atoms in a linear system, the electron can be treated as a free particle which is constrained to move along a straight line, i.e., a particle in a one-dimensional box. The Schrödinger equation for a free particle in a one-dimensional box is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2mE}{h^2} \psi = 0 \quad (1)$$

$\psi$  is the wave function,  $m$  is the mass of the particle,  $E$  is the energy, and  $h$  is Planck's constant. The solution to Equation (1) is

$$\psi = \sin \sqrt{\frac{8\pi^2 mE}{h^2}} x = \sin \theta \quad (2)$$

where

$$\theta \equiv \sqrt{\frac{8\pi^2 mE}{h^2}} x \quad (3)$$

The boundary conditions require that  $\psi = 0$  at  $x = 0$  and  $x = \ell$ , where  $\ell$  is the path length, i.e., the probability of finding the electron outside of the defined path is zero. Therefore

$$\sin \sqrt{\frac{8\pi^2 mE}{h^2}} \ell = 0 \quad (4)$$

which requires that

$$\sqrt{\frac{8\pi^2 mE}{h^2}} \ell = n\pi \quad (5)$$

where  $n$  is an integer. We can now solve for the energy,

$$E_L = \frac{n^2 h^2}{8m\ell^2} \quad (6)$$

(The subscript  $L$  denotes a linear path.)

Now let us consider the case of a free particle moving along a circle. The circular path length  $\ell$  must equal an integral number of wavelengths, since the wave function must be single-valued and continuous. If  $\theta$  is the angle the particle subtends when moving a distance  $x$  along the circle, then

$$\frac{x}{\ell} = \frac{\theta}{2\pi} \quad (7)$$

or

$$\theta = \frac{2\pi x}{\ell} \quad (8)$$

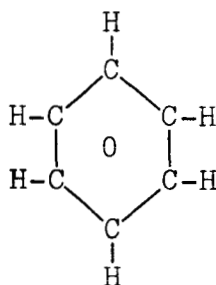
which results in

$$E_C = \frac{n^2 h^2}{2m\ell^2} \quad (9)$$

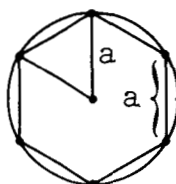
(The subscript  $C$  denotes a circular path.)

$E_L$  and  $E_C$  correspond to the electron's contribution to the internal energy of the molecule in linear and cyclic systems. Stability is a function of the internal energy; the lower the energy the more stable the system. Equation (5) indicates that for an electron moving along a linear path the contribution to the internal energy is inversely proportional to the path length accessible to the electron. If an electron is localized between two atoms its contribution to the internal energy of the system is much greater than if it were delocalized over a few atoms. A linearly conjugated system is therefore more stable than a system in which delocalization does not occur.

For the cyclic case benzene will be used as an example. The molecular structure of benzene,  $C_6H_6$ , can be represented as



where the circle in the ring is the chemical notation for aromaticity. Let us compare two cases: (1) the six electrons are completely delocalized, and (2) each electron is localized between two carbon atoms.



distance between two carbon atoms =  $a$   
circular path length =  $2\pi a$

Case (1):

$$E_C = \frac{n^2 h^2}{2m\ell^2} = \frac{n^2 h^2}{2m(2\pi a)^2} = \frac{n^2 h^2}{8\pi^2 m a^2} \text{ per electron} \quad (10)$$

For six electrons the contribution is

$$E_C = \frac{6}{8} \frac{n^2 h^2}{\pi^2 m a^2} \quad (11)$$

Case (2):

$$E_L = \frac{n^2 h^2}{8ma^2} \quad (12)$$

and for six electrons

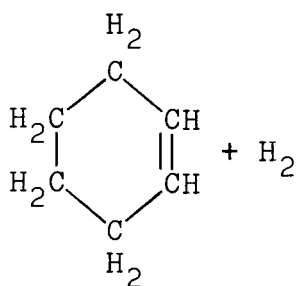
$$E_L = \frac{6n^2 h^2}{8ma^2} \quad (13)$$

Comparing the contributions to the internal energy:

$$\begin{aligned} E_L - E_C &= \frac{6}{8} \frac{n^2 h^2}{ma^2} - \frac{6}{8} \frac{n^2 h^2}{\pi^2 ma^2} \\ &= \frac{6}{8} \frac{n^2 h^2}{ma^2} \left[ 1 - \frac{1}{\pi^2} \right] > 0 \end{aligned} \quad (14)$$

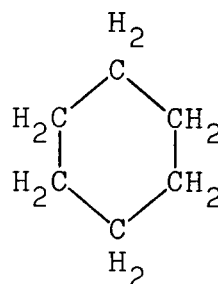
This shows that cyclic aromatic systems contribute less to the internal energy than do linear systems, and, therefore, we should expect cyclic aromatic systems to be the more stable.

We next consider an example of how the presence of aromatic groups in the polymer backbone results in a thermally stable product. Considering the hydrogenation reaction:



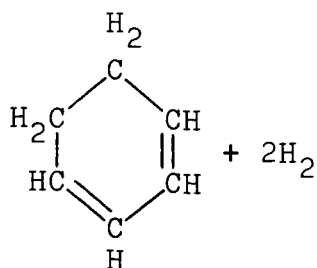
cyclohexene

Catalyst



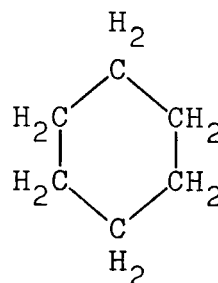
cyclohexane

$$\Delta H = -28.6 \frac{\text{kcal}}{\text{mole}}$$



1,3-cyclohexadiene

Catalyst

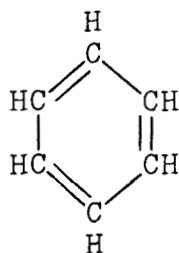


cyclohexane

$$\Delta H = -55.4 \frac{\text{kcal}}{\text{mole}}$$



These reactions indicate that the energy released upon hydrogenation is  $\sim 28$  kcal/mole per double bond. If we now consider the structure of benzene to be



we expect  $\Delta H_{\text{hydrogenation}}$  to be three times that for a single double bond, i.e.,  $\sim 86$  kcal/mole of benzene. However,  $\Delta H$  observed is  $-50$  kcal/mole, 36 kcal lower than expected. (A similar anomaly results when the heats of combustion are compared.)

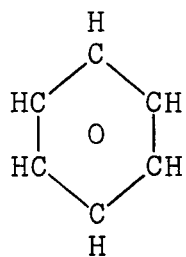
The experimental observation that the energy release for benzene is 36 kcal/mole lower than expected is in accord with quantum mechanical calculations of the stabilization due to the delocalization of the  $\pi$  clouds in benzene, which predict  $E_{\text{stabilization}} \sim 36$  kcal/mole. Qualitatively this means that before a chemical process (e.g., hydrogenation or combustion) can begin, the stabilizing  $\pi$  clouds must be disrupted and the stabilizing influence eliminated; the molecule must be "primed" for reaction.

#### SOME AROMATIC SYSTEMS

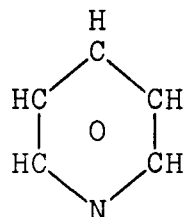
Aromatic molecules must be planar to permit the  $\pi$  orbitals to overlap. Benzene and its derivatives are the most familiar aromatic compounds; but they are by no means the only aromatic systems. Five-, six-, and seven-membered ring compounds can be aromatic. They are ideally suited since they provide the necessary number of electrons, and rings of this size easily fulfill the geometric requirements. This allows us to state a general definition for aromaticity:

"Aromatic compounds are those whose molecules contain cyclic  $\pi$  clouds above and below the plane of the molecule." [11]

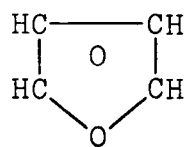
Some aromatic compounds are listed below. The circle inside the rings is the common chemical notation indicating aromaticity. Aromatic systems may contain other species as well as carbon, e.g., nitrogen. Molecules of this type are called heterocyclic.



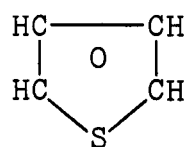
benzene



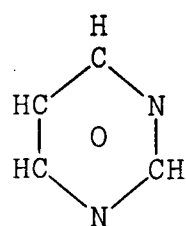
pyridine



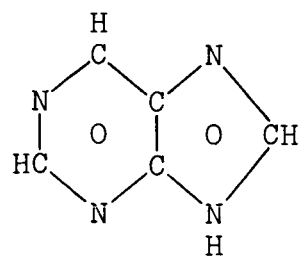
furan



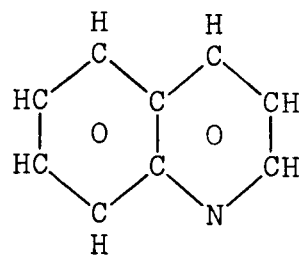
thiophene



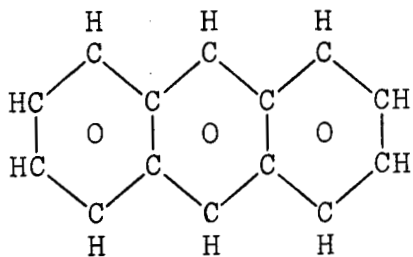
pyrimidine



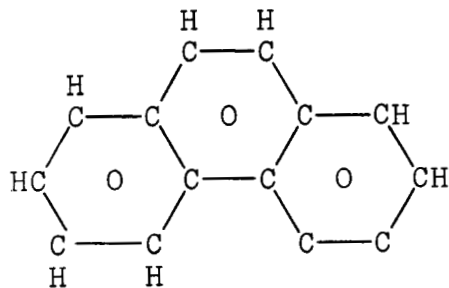
purine



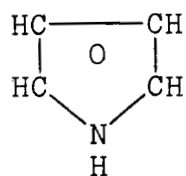
quinoline



anthracene

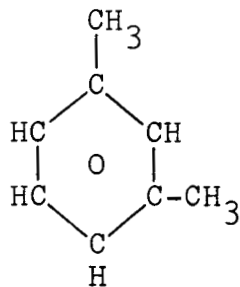


phenanthrene

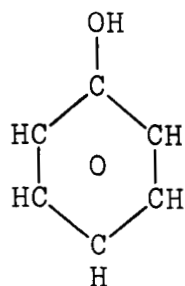


pyrrole

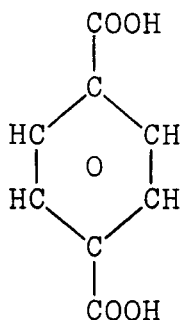
Derivatives, i.e., replacement of the hydrogen atoms by more complex groups, of these aromatic compounds are also aromatic, e.g.,



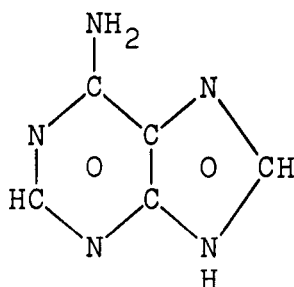
meta-xylene



phenol



terephthalic acid



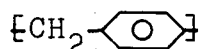
adenine

## COMPARISON OF THE BEHAVIOR OF AROMATIC AND NON-AROMATIC POLYMERS

In the case of pyrolysis of polymers a similar argument may be used to explain why polymers containing aromatic moieties in the backbone are more thermally stable than the non-aromatics. When polymers are pyrolyzed bonds are broken and lower molecular weight products are released. For non-aromatics the absorbed heat is used primarily in breaking the  $\sigma$ -bonds. However, for aromatic polymers a considerable amount of energy must be consumed in disrupting the  $\pi$  cloud and thereby destabilizing the molecule sufficiently for the bond-breaking process to occur. For example, if we consider the parameter  $T_h$ , the temperature corresponding to a 50% loss of weight of a given polymer sample in 40-45 minutes of heating we can see the correlation. [5]

<u>POLYMER</u>	<u><math>T_h</math>, °C</u>	
Polystyrene		
$\left[ \text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_n$	364	(contains an aromatic group, but not in the carbon backbone)
Polypropylene		
$\left[ \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} \right]_n$	387	

Polybenzyl



430

Poly-p-xylyl



432

Thus, polymers with aromatic groups in the carbon backbone exhibit a significant increase in  $T_h$  as compared with non-aromatics (even though the latter may contain aromatic side-chains).

Another technique employed in determining thermal stability is to measure the rate of weight loss as a function of temperature increase. Polymers containing aromatic groups in the backbone exhibit a slower weight loss than the non-aromatics. Figure 6 shows that polybenzyl  $\{ \text{CH}_2 - \text{C}_6\text{H}_4 \}_n$  and poly-p-xylyl  $\{ \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 \}_n$  are considerably more thermally stable than the non-aromatics with which they are compared. (Teflon  $\{ \text{CF}_2 \}_n$  is non-aromatic; however, it is especially stable due to the presence of the fluorine atoms.)

Recent attempts to polymerize more complex aromatic monomers which result in an almost entirely aromatic backbone have been fairly successful. One of the products is polybenzimidazole (PBI),  $\{ \text{C}_6\text{H}_4 - \text{C}_2\text{H}_2\text{N}_2 \}_n$ . Figure 7 shows a

thermal decomposition curve derived from the manufacturer's data.<sup>[10]</sup> By comparing Figures 6 and 7 it can be seen that the polybenzimidazole is even more stable than polybenzyl. PBI is now available commercially, and has been used for some applications in the Apollo spacecraft.

More recent efforts have been focused on polyquinoxalines; Figure 8 shows the thermal behavior of one of the polyquinoxalines.<sup>[8]</sup> The polyquinoxalines are totally aromatic and the synthetic techniques have resulted in ladder polymers which are highly ordered and which have no available reactive sites since they are all involved in bond formation. Therefore, these ladder polymers have greater stability than linear or randomly cross-linked polymers.

A major difficulty encountered with the polyquinoxalines has been the rigidity of the plastics resulting from the highly

ordered molecular structures. Attempts to correct this by replacing some of the carbon atoms in the backbone by oxygen, nitrogen, or sulfur have been successful; the resulting materials have good plastic properties and still retain their thermal stability. Present work on the polyquinoxalines, still in the developmental stage, is also concerned with producing higher molecular weight products (since the thermal stability is enhanced by higher molecular weights).

It is thought by some people in the field that  $\sim 700^{\circ}\text{C}$  ( $1300^{\circ}\text{F}$ ) is an upper temperature limit for aromatic polymers to resist degradation in inert atmospheres. However, some recent studies have suggested that when these polymers degrade thermally the solid residue may represent an even more stable polymeric material. The situation will have to be thoroughly investigated.

Many thermally resistant aromatic materials are presently on the market. There are, for example, KAPTON - an aromatic polyimide, VESPEL - also a polyimide, and some self-extinguishing polyphenylene oxide resins.

#### FUTURE EXPECTATIONS AND NEEDS

It seems reasonable to expect that many more thermally resistant materials will be available within the next few years. In addition to polyaromatics there may be carboranes and inorganic polymers. Since flammability properties are intimately related to pyrolytic behavior it is felt that the number of available non-flammable or very slow burning materials will greatly increase in the near future.

There is, however, one vital gap of knowledge in this field. It appears that very few, if any, studies on pyrolytic behavior in  $\text{O}_2$ -containing atmospheres have been made. It is both desirable and necessary that these studies be initiated so that data on the behavior of these materials in  $\text{O}_2$  will be readily available. This information would be of great assistance in defining materials selection criteria and perhaps also in the design of future fire detection systems.



2031-MVD-tfb

M. V. Drickman

## BELLCOMM, INC.

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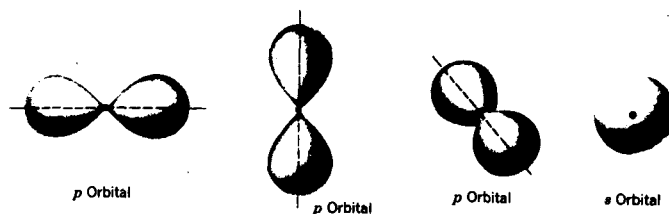


FIGURE 1 - THE  $2p$  AND  $2s$  HYDROGENIC ORBITALS

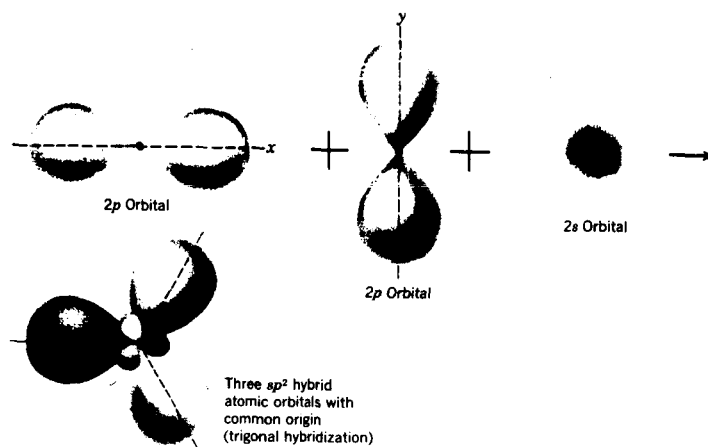


FIGURE 2 - FORMATION  $sp^2$  HYBRID ORBITAL

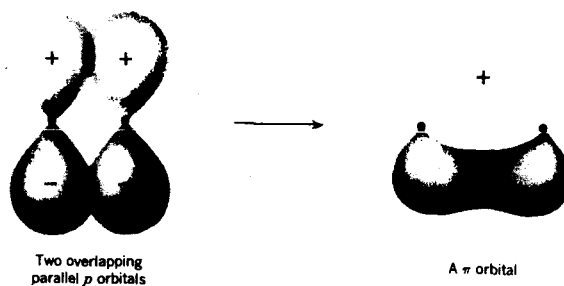


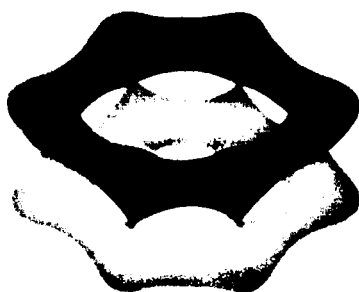
FIGURE 3 - COMBINATION OF PARALLEL  $p$  ORBITALS TO FORM A  $\pi$  ORBITAL

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FIGURE 4 -  $\pi$ -ORBITALS BUTADIENE



First benzene  $\pi$  orbital



FIGURE 5 -  $\pi$ -ORBITALS IN BENZENE

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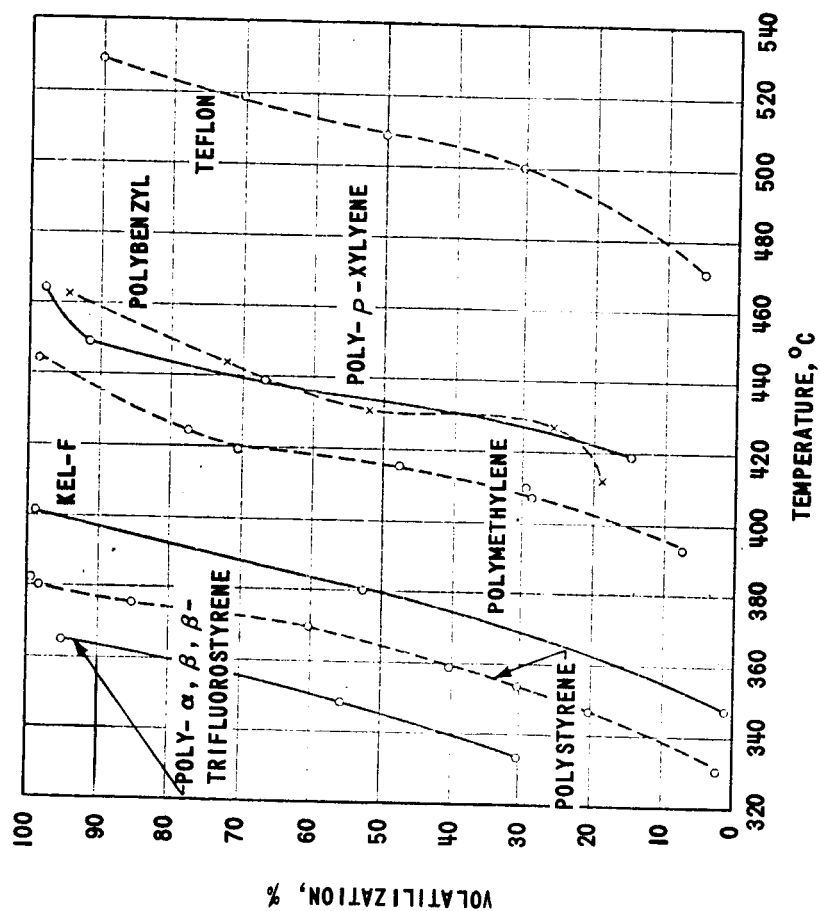


FIGURE 6 - RELATIVE THERMAL STABILITY OF POLYBENZYL AND POLY-P-XYLENE COMPARED WITH THAT OF OTHER POLYMERS

FIGURE 6 IS FROM "THERMAL DEGRADATION OF ORGANIC POLYMERS" BY S. L. MADORSKY. COPYRIGHT 1964 BY JOHN WILEY AND SONS, INC. USED WITH THE PERMISSION OF THE PUBLISHER.

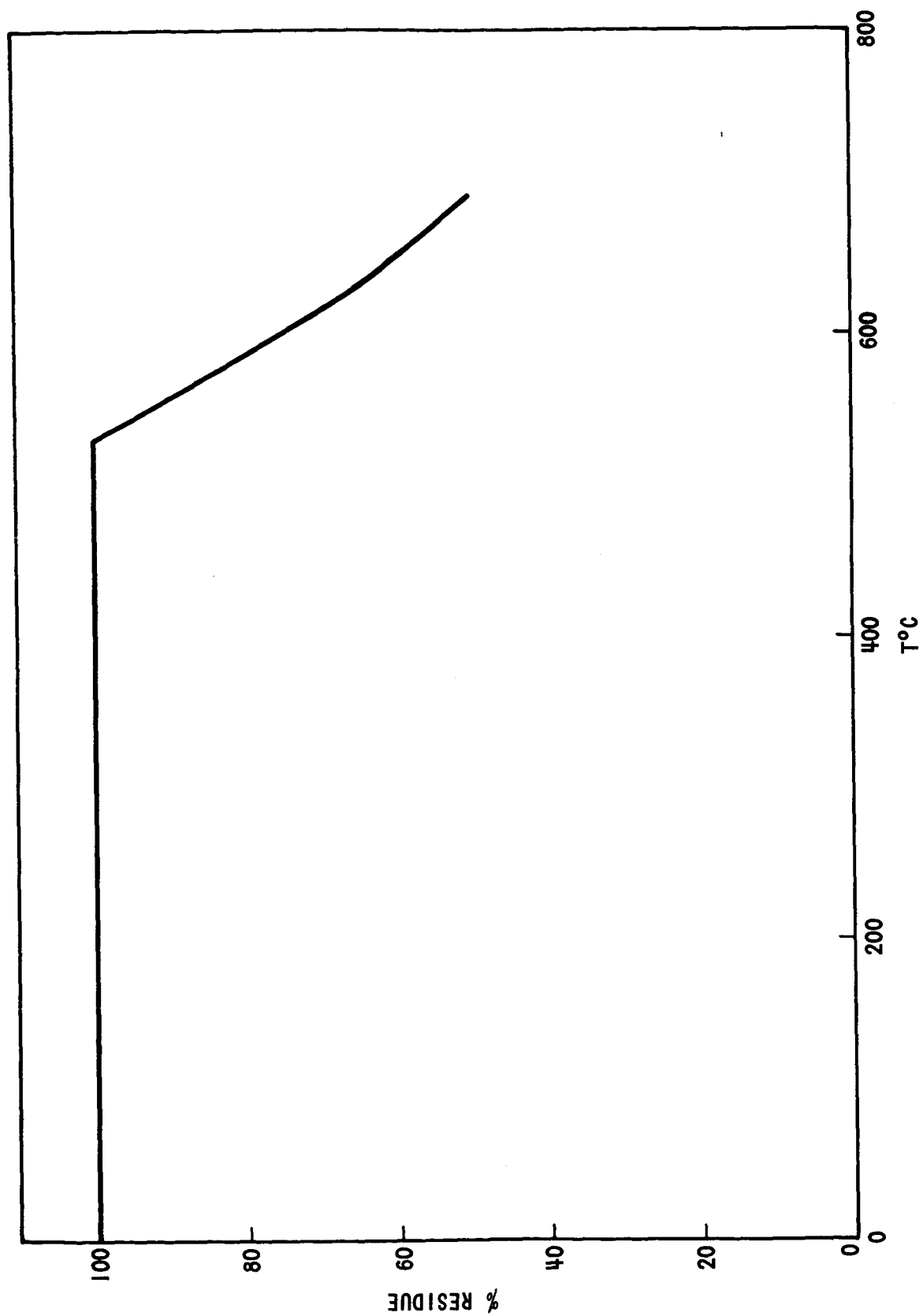


FIGURE 7 - THERMAL DEGRADATION OF POLYBENZIMIDAZOLE IN AIR

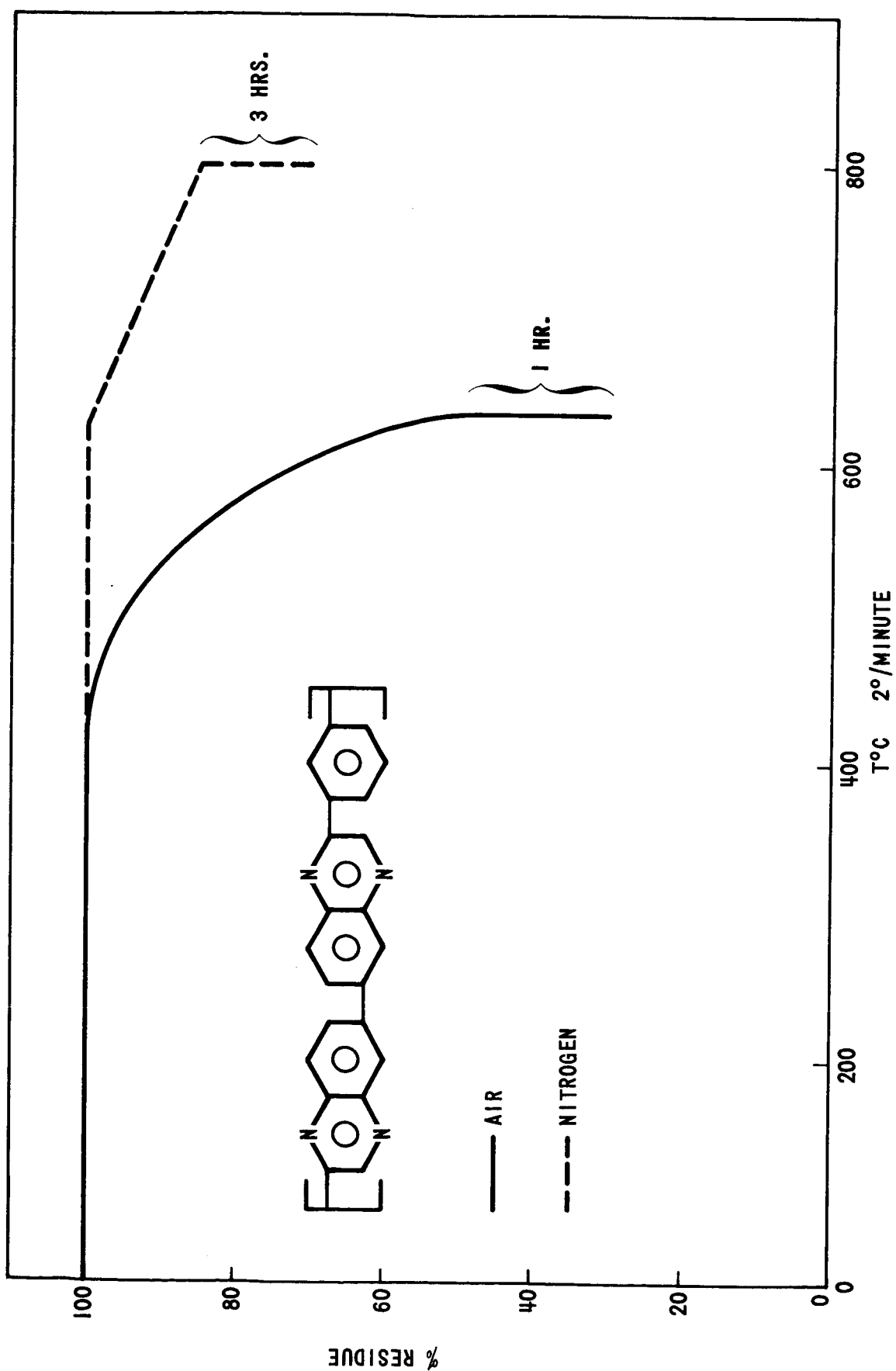


FIGURE 8 - THERMAL DEGRADATION OF POLYQUINOXALINE

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